Environmental Remediation Group

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SENT VIA ELECTRONIC MAIL

November 26, 2019

Ms. Melanie Morash
U. S. Environmental Protection Agency (USEPA), Region 1
5 Post Office Square, Suite 100,
Mail Stop OSRR07-4, Boston, MA 02109-3912

RE: Updated Ambient Water Quality Criterion (AWQC) for Ammonia
Olin Chemical Superfund Site (OCSS; "Site") – Wilmington, MA

Dear Ms. Morash:

As a follow-up to the discussions between USEPA and Olin, and as requested by USEPA at the October 2, 2019 meeting, transmitted herewith is a technical memorandum that recommends an updated site-specific ammonia Ambient Water Quality Criterion (AWQC). The recommended ammonia AWQC is for aquatic receptors, more specifically, as recommended by USEPA at the meeting, a Criterion Continuous Concentration (CCC) that reflects no early life stage fish, absence of mussels, and site-specific pH and surface water temperature representative of the spring season. This updated AWQC for ammonia will be used in evaluating water quality in the East Ditch adjacent to the Site and the South Ditch at the OCSS.

Let us know if you have any questions.

Sincerely,
OLIN CORPORATION

James M. Cashwell
Director, Environmental Remediation

Enclosure

cc: Chinny Esakkiperumal (Olin)
Libby Bowen (Wood)

Wood Environment & Infrastructure Solutions, Inc.
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Third Floor
Chelmsford, MA 01824
USA
T: 978-692-9090

Technical Memorandum

To:	Chinny Esakkiperumal		
From:	Michael Murphy	**Reviewer:**	Elizabeth Bowen
cc:	Nelson Walter	**Wood File No.:**	6107190016
Date:	November 25, 2019		
Re:	**Site-Specific AWQC for Ammonia – Olin Chemical Superfund Site**		

1.0 Introduction and Purpose

This technical memorandum has been prepared in response to discussions and a request from the United States Environmental Protection Agency (USEPA) at the October 2, 2019 Olin Chemical Superfund Site (OCSS) meeting at USEPA's offices. As requested by USEPA, this memorandum recommends an updated site-specific ammonia Ambient Water Quality Criterion (AWQC) for aquatic receptors, more specifically, a Criterion Continuous Concentration (CCC) that reflects no early life stage fish, absence of mussels, and site-specific pH and surface water temperature representative of the spring season. This updated AWQC will be used in evaluating water quality in the East Ditch adjacent to the 51 Eames Street property (the Property) and South Ditch at the OCSS. Much of the information and procedures used in developing the recommended CCC has been obtained from Appendix N of the USEPA *Aquatic Life Ambient Water Quality Criteria for Ammonia – Freshwater 2013* (USEPA, 2013), hereafter referred to as "the Criteria Document."

In the October 2, 2019 meeting, there was a consensus that it is appropriate that the site-specific AWQC for ammonia does not need to be protective of mussels or early life stages for fish since neither mussels nor fish are present in these ditches and the habitat characteristics are not suitable for those organisms. Part of that consensus was agreement that a CCC of 7.1 mg/L total ammonia nitrogen (TAN) assuming a pH of 7 and temperature of 20 degrees Celsius (as shown in Table N-9 of the Criteria Document) was an appropriate starting point for further adjustment of the CCC. Table N-9 of the Criteria Document (*Temperature and pH-Dependent Values of the CCC (Chronic Criterion Magnitude[1]) – Mussels Absent and Early Life Stage (ELS) Protection Not Necessary*) is included in **Attachment A** of this memorandum. USEPA recommended that a site-specific AWQC should be developed to reflect site-specific surface water pH and temperature.

The recommended total ammonia nitrogen AWQC for East Ditch adjacent to the Property and South Ditch surface water are 14 milligrams/liter (mg/L) and 19 mg/L, respectively.

[1] The chronic AWQC is the Criterion Continuous Concentration (CCC). Within the Criteria Document, EPA often refers to the CCC as the Chronic Criterion Magnitude. This latter term should not be confused with the acute AWQC which is the Criterion Maximum Concentration (CMC).

2.0 Guidance for Derivation of Site-Specific Ammonia AWQC

The Criteria Document provides specific procedures and recommendations for deriving a site-specific AWQC for ammonia (particularly in the appendices of that document). The following subsections of this memorandum discuss site-specific factors to be considered and also provide a summary of relevant information concerning the speciation of ammonia in water and the relative toxicity to aquatic life of the ammonia species. These ammonia species include NH_3 (un-ionized ammonia) and NH_4^+ (ionized ammonia – also referred to as ammonium ion). As reported in the Criteria Document, un-ionized ammonia (NH_3) is the species of ammonia that is toxic to aquatic life and ionized ammonia (NH_4^+) is considered to be essentially non-toxic to aquatic organisms.

Table N-9 of the Criteria Document is particularly relevant to the derivation of a site-specific CCC for ammonia in surface water of the East Ditch and South Ditch. This table identifies CCC values over a range of surface water temperatures (0 – 30 degrees Celsius) and pH values (6.5 – 9.0).

2.1 Site-specific factors to be considered and impact on CCC

Several site surface water characteristics may potentially affect the concentration protective of aquatic receptors and/or the toxicity to aquatic receptors of ammonia measured as TAN. These factors include the presence or absence of certain potential sensitive aquatic receptors, surface water pH, and surface water temperature.

2.2 pH-dependent speciation of ammonia

As described on pages 6 and 7 of the Criteria Document, ammonia in water is characterized by an equilibrium between un-ionized ammonia and ammonium ion. The equilibrium and the ratio of the concentrations of these two ammonia forms in surface water is determined by the pH of the water. **Attachment B** of this memorandum includes a copy of pages 6 and 7 of the Criteria Document which include a figure that shows the relative distribution of the two forms of ammonia over a range pH values from approximately 5.5 to approximately 10.5 at a temperature of 25 degrees Celsius.

As shown in this figure, the two forms are present at approximately 50% of the total ammonia concentration at pH 9.2. As pH decreases from 9.2, the ionized form (NH_4^+) becomes predominant and the toxic ionized form (NH_3) concentrations are markedly reduced. At pH 7, the ionized form accounts for more than 99% of the total ammonia concentration in the water and the toxic form less than 1% of the total concentration. As the pH decreases further, the ratio of concentrations of the ionized to un-ionized forms increases (the ratio increases 10-fold for each decrease of one logarithmic pH unit). At pH of approximately 6.3, the ratio of concentrations of NH_4^+ to NH_3 is approximately 1,000:1 (the toxic NH_3 form represents only approximately 0.1% of the total ammonia concentration).

Temperature has a much weaker influence on speciation. In general, the ratio of NH_3 to NH_4^+ increases 10-fold for each rise of a single pH unit, but by a factor of two for each 10 degree Celsius rise in temperature.

Simply put, toxicity increases as pH and temperature (and therefore un-ionized ammonia NH_3 concentration) increase.

3.0 Site-Specific Characteristics

3.1 Absence of fish and mussels in East Ditch and South Ditch surface water

Wood scientists have inspected the South Ditch during monthly inspections and Olin personnel have inspected the South Ditch weekly for more than 18 years. Wood biologists have also inspected the East Ditch on numerous occasions in each of the seasons of the year. Neither fish nor mussels have been observed in either of the ditches. USEPA representatives concurred at the October 2, 2019 meeting that the absence of fish and mussels is an appropriate basis for deriving a site-specific ammonia AWQC for the two ditches.

3.2 Spring surface water temperature -East Ditch and South Ditch

At the October 2, 2019 meeting, USEPA recommended the use of spring-time surface water temperature to derive the site-specific ammonia AWQC since aquatic invertebrates are present during that season. The Interim Response Steps Work Plan (IRSWP) surface water monitoring program has included quarterly sampling and analysis of surface water samples from the East Ditch (sample location ISCO-3) and the South Ditch (sample locations (ISCO-1, ISCO-2, PZ-16RRR, PZ-17RRR, PZ-18R, and SD-17). **Attachment C** includes a figure from the July 2019 Semi-Annual Status Report showing the IRSWP surface water sample locations. The surface water samples from that program have been analyzed for a targeted suite of metals and inorganics and field parameters including temperature and pH were also measured for each sample collected. **Table 1** includes and summarizes the temperature and pH data for surface water samples during the spring sampling events from 2013 through 2019.

Table 1 includes the surface water temperature readings for the first quarter (late March and early April) samples collected in the East Ditch (at location ISCO-3) and in the South Ditch (at locations ISCO-1, ISCO-2, PZ-16RRR, PZ-17RRR, PZ-18R, and SD-17). The average spring surface water temperatures for the East Ditch and South Ditch are 9.20 degrees Celsius and 6.92 degrees Celsius, respectively.

3.3 Spring surface water pH - East Ditch and South Ditch

Table 1 includes the surface water pH readings for the first quarter (late March and early April) samples collected in the East Ditch (at location ISCO-3) and in the South Ditch (at locations ISCO-1, ISCO-2, PZ-16RRR, PZ-17RRR, PZ-18R, and SD-17) The average spring surface water pH for the East Ditch and South Ditch are 7.13 and 6.92, respectively.

4.0 Site-Specific Ammonia Criterion Continuous Concentration (CCC)

The information presented in Section 3.0 concerning the presence or absence of certain potential sensitive aquatic receptors, surface water pH, and surface water temperature for the East Ditch and South Ditch have been applied to the matrix in Table N-9 of the Criteria Document (reproduced here as Attachment A) to identify site-specific ammonia CCCs. The table presents temperature in whole degrees and pH in tenths of a pH unit. Site specific values have been rounded to match this convention. For the East Ditch adjacent to the Property, using the temperature of 9.20 (rounded to 9) and the pH of 7.13 (rounded to 7.1), the site-specific CCC would be 14 mg/L TAN. For the South Ditch, using the temperature of 6.92 (rounded to 7) and the pH of 6.45 (rounded to 6.5 for convenience), the site-specific CCC would be 19 mg/L TAN.

5.0 CONCLUSIONS

The recommended site-specific chronic AWQ for ammonia in surface water of the East Ditch adjacent to the Property is 14 mg/L, measured as total ammonia nitrogen.

The recommended site-specific chronic AWQ for ammonia in surface water of the South Ditch is 19 mg/L, measured as total ammonia nitrogen.

6.0 References

USEPA, 2013. *Aquatic Life Ambient Water Quality Criteria for Ammonia – Freshwater 2013,* EPA 822-R-18-002, April.

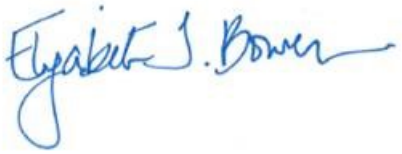
Sincerely,

Wood Environment & Infrastructure Solutions, Inc.

Prepared by:

Michael Murphy
Principal Risk Assessor

Reviewed by:



Elizabeth T. Bowen
Associate Project Manager

TABLES

Table 1
Summary of Temperature and pH - East and South Ditches Surface Water
Slurry Wall/Cap Monitoring Program
Olin Chemical Superfund Site
Wilmington, Massachusetts

Temperature (° C)							
Sample Date	**East Ditch**	**South Ditch**					
	ISCO3	**ISCO1**	**ISCO2**	**PZ-16RRR**	**PZ-17RRR**	**PZ-18R**	**SD-17**
3/21/2013	2.40	3.14	1.48	1.89	2.47	3.28	2.52
4/2/2014	8.53	7.17	6.14	6.20	6.29	7.23	6.70
4/14/2015	11.41	11.65	11.02	11.26	10.85	11.68	10.84
3/22/2016	-	5.60	4.07	4.16	4.96	5.77	4.96
3/30/2017	9.33	5.90	5.99	5.47	5.51	5.21	5.80
4/12/2018	9.19	8.52	7.17	8.85	7.54	8.87	7.47
4/2/2019	14.34	8.57	9.07	10.41	9.85	9.10	10.13
Mean:	9.20	7.22	6.42	6.89	6.78	7.31	6.92
East Ditch Mean:	9.20	South Ditch Mean:		6.92			

pH (standard units)							
Sample Date	**East Ditch**	**South Ditch**					
	ISCO3	**ISCO1**	**ISCO2**	**PZ-16RRR**	**PZ-17RRR**	**PZ-18R**	**SD-17**
3/21/2013	6.90	6.26	6.42	5.88	6.12	6.13	6.20
4/2/2014	6.89	6.01	6.30	6.00	5.96	6.04	5.95
4/14/2015	6.56	5.72	6.18	5.93	5.91	5.80	5.82
3/22/2016	-	5.95	5.97	6.61	7.30	6.03	7.29
3/30/2017	6.67	5.85	6.27	6.71	6.43	5.73	6.44
4/12/2018	8.93	7.03	8.88	8.78	8.56	7.48	8.41
4/2/2019	6.82	6.28	6.24	6.07	5.95	5.94	5.90
Mean:	7.13	6.16	6.61	6.57	6.60	6.16	6.57
East Ditch Mean:	7.13	South Ditch Mean:		6.45			

Notes:
- = no sample collected

Prepared by: MJM 10/17/19
Checked by: JP 11/19/19

ATTACHMENT A

TABLE N-9 FROM USEPA *AQUATIC LIFE AMBIENT WATER QUALITY CRITERIA FOR AMMONIA – FRESHWATER 2013*

Table N.9. Temperature and pH-Dependent Values of the CCC (Chronic Criterion Magnitude) – Mussels Absent and Early Life Stage (ELS) Protection not Necessary.

	Temperature (°C)																							
pH	0-7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
6.5	19	17	16	15	14	13	13	12	11	10	9.7	9.1	8.5	8.0	7.5	7.0	6.6	6.2	5.8	5.4	5.1	4.8	4.5	4.2
6.6	18	17	16	15	14	13	12	12	11	10	9.6	9.0	8.4	7.9	7.4	6.9	6.5	6.1	5.7	5.4	5.0	4.7	4.4	4.1
6.7	18	17	16	15	14	13	12	11	11	10	9.4	8.8	8.3	7.7	7.3	6.8	6.4	6.0	5.6	5.3	4.9	4.6	4.3	4.1
6.8	17	16	15	14	14	13	12	11	10	9.8	9.2	8.6	8.1	7.6	7.1	6.7	6.2	5.8	5.5	5.1	4.8	4.5	4.2	4.0
6.9	17	16	15	14	13	12	12	11	10	9.5	8.9	8.4	7.8	7.4	6.9	6.5	6.1	5.7	5.3	5.0	4.7	4.4	4.1	3.9
7.0	16	15	14	14	13	12	11	10	9.8	9.2	8.6	8.1	7.6	**7.1**	6.7	6.2	5.9	5.5	5.1	4.8	4.5	4.2	4.0	3.7
7.1	16	15	14	13	12	11	11	10	9.4	8.8	8.3	7.7	7.3	6.8	6.4	6.0	5.6	5.3	4.9	4.6	4.3	4.1	3.8	3.6
7.2	15	14	13	12	12	11	10	9.5	9.0	8.4	7.9	7.4	6.9	6.5	6.1	5.7	5.3	5.0	4.7	4.4	4.1	3.9	3.6	3.4
7.3	14	13	12	12	11	10	9.6	9.0	8.4	7.9	7.4	6.9	6.5	6.1	5.7	5.4	5.0	4.7	4.4	4.1	3.9	3.6	3.4	3.2
7.4	13	12	12	11	10	9.5	9.0	8.4	7.9	7.4	6.9	6.5	6.1	5.7	5.3	5.0	4.7	4.4	4.1	3.9	3.6	3.4	3.2	3.0
7.5	12	11	11	10	9.4	8.8	8.2	7.7	7.2	6.8	6.4	6.0	5.6	5.2	4.9	4.6	4.3	4.1	3.8	3.6	3.3	3.1	2.9	2.8
7.6	11	10	10	9.1	8.5	8.0	7.5	7.0	6.6	6.2	5.8	5.4	5.1	4.8	4.5	4.2	3.9	3.7	3.5	3.2	3.0	2.9	2.7	2.5
7.7	9.9	9.3	8.7	8.1	7.7	7.2	6.8	6.3	5.9	5.6	5.2	4.9	4.6	4.3	4.0	3.8	3.5	3.3	3.1	2.9	2.7	2.6	2.4	2.3
7.8	8.8	8.3	7.8	7.3	6.8	6.4	6.0	5.6	5.3	5.0	4.6	4.4	4.1	3.8	3.6	3.4	3.2	3.0	2.8	2.6	2.4	2.3	2.1	2.0
7.9	7.8	7.3	6.8	6.4	6.0	5.6	5.3	5.0	4.6	4.4	4.1	3.8	3.6	3.4	3.2	3.0	2.8	2.6	2.4	2.3	2.1	2.0	1.9	1.8
8.0	6.8	6.3	6.0	5.6	5.2	4.9	4.6	4.3	4.0	3.8	3.6	3.3	3.1	2.9	2.7	2.6	2.4	2.3	2.1	2.0	1.9	1.7	1.6	1.5
8.1	5.8	5.5	5.1	4.8	4.5	4.2	4.0	3.7	3.5	3.3	3.1	2.9	2.7	2.5	2.4	2.2	2.1	2.0	1.8	1.7	1.6	1.5	1.4	1.3
8.2	5.0	4.7	4.4	4.1	3.9	3.6	3.4	3.2	3.0	2.8	2.6	2.5	2.3	2.2	2.0	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.1
8.3	4.2	4.0	3.7	3.5	3.3	3.1	2.9	2.7	2.5	2.4	2.2	2.1	2.0	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.2	1.1	1.0	0.96
8.4	3.6	3.4	3.2	3.0	2.8	2.6	2.4	2.3	2.1	2.0	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.1	1.1	0.99	0.92	0.87	0.81
8.5	3.0	2.8	2.7	2.5	2.3	2.2	2.1	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.2	1.1	1.0	0.95	0.89	0.83	0.78	0.73	0.69
8.6	2.6	2.4	2.2	2.1	2.0	1.9	1.7	1.6	1.5	1.4	1.3	1.3	1.2	1.1	1.0	0.97	0.91	0.85	0.80	0.75	0.70	0.66	0.62	0.58
8.7	2.2	2.0	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.1	1.1	1.0	0.93	0.88	0.82	0.77	0.72	0.68	0.63	0.60	0.56	0.52	0.49
8.8	1.8	1.7	1.6	1.5	1.4	1.3	1.3	1.2	1.1	1.0	0.96	0.90	0.85	0.79	0.74	0.70	0.65	0.61	0.58	0.54	0.51	0.47	0.44	0.42
8.9	1.6	1.5	1.4	1.3	1.2	1.1	1.1	1.0	0.94	0.88	0.82	0.77	0.72	0.68	0.64	0.60	0.56	0.52	0.49	0.46	0.43	0.40	0.38	0.36
9.0	1.4	1.3	1.2	1.1	1.0	0.98	0.92	0.86	0.81	0.76	0.71	0.66	0.62	0.58	0.55	0.51	0.48	0.45	0.42	0.40	0.37	0.35	0.33	0.31

ATTACHMENT B

FATE AND TRANSPORT PAGES EXTRACTED FROM USEPA *AQUATIC LIFE AMBIENT WATER QUALITY CRITERIA FOR AMMONIA – FRESHWATER 2013*

extensively in order to keep the concentrations of ammonia in surface waters from being unacceptably high. In 2011, there were approximately 4.7 million pounds (lbs.) of ammonia documented as discharged from all reporting industries to surface waters (U.S. EPA 2011). In 2010, industrial releases of ammonia to ten large aquatic ecosystems (e.g., Chesapeake Bay, Puget Sound, Great Lakes) were reported to total approximately 1.3 million lbs. (U.S. EPA 2010).

Environmental Fate and Transport of Ammonia in the Aquatic Environment

Ammonia (NH_3) is formed in the natural environment by the fixation of atmospheric nitrogen and hydrogen by diazotrophic microbes, such as cyanobacteria (Latysheva et al. 2012). Trace amounts are also produced by lightning (Noxon 1976). Decomposition of manure, dead plants and animals by bacteria in the aquatic and terrestrial environments produce ammonia and other ammonium compounds through conversion of nitrogen during decomposition of tissues in a process called ammonification (ATSDR 2004; Sylvia 2005). In the aquatic environment, ammonia is also produced and excreted by fish. The chemical form of ammonia in water consists of two species, the more abundant of which is the ammonium ion (NH_4^+) and the less abundant of which is the non-dissociated or unionized ammonia (NH_3) molecule; the ratio of these species in a given aqueous solution is dependent upon both pH and temperature (Emerson et al. 1975; Erickson 1985; Thurston 1988; Whitfield 1974; Wood 1993). Chemically, ammonia in an aqueous medium behaves as a moderately strong base with pK_a values ranging from approximately 9 to slightly above 10 as a function of temperature and ionic strength (Emerson et al. 1975; Whitfield 1974). In general, the ratio of unionized ammonia to ammonium ion in fresh water increases by 10-fold for each rise of a single pH unit, and by approximately two-fold for each 10°C rise in temperature from 0-30°C (Erickson 1985). Basically, as values of pH and temperature tend to increase, the concentration of NH_3 increases and the concentration of NH_4^+ decreases.

The ionized ammonium ion (NH_4^+) and unionized ammonia molecule (NH_3) are interrelated through the chemical equilibrium $NH_4^+ - OH^- \leftrightarrow NH_3 \cdot H_2O \leftrightarrow NH_3 + H_2O$ (Emerson et al. 1975; Russo 1985). The concentration of total ammonia (often expressed on the basis of nitrogen as total ammonia nitrogen or TAN) is the sum of NH_4^+ and NH_3 concentrations. It is total ammonia that is analytically measured in water samples. To estimate the relative

concentrations of NH_4^+ and NH_3 from total ammonia, Emerson et al.'s (1975) formulas are recommended (Adams and Bealing 1994; Alabaster and Lloyd 1980; Richardson 1997; Russo 1985). Figure 1 (below) shows the chemical speciation of ammonia over a range of pH levels in ambient waters at 25°C. It depicts the 10-fold increase in the ratio of unionized ammonia to ammonium ion in fresh water for each rise of a single pH unit as described above. This increase in unionized ammonia with increased pH is one hypothesis explaining why toxicity of total ammonia increases as pH increases.

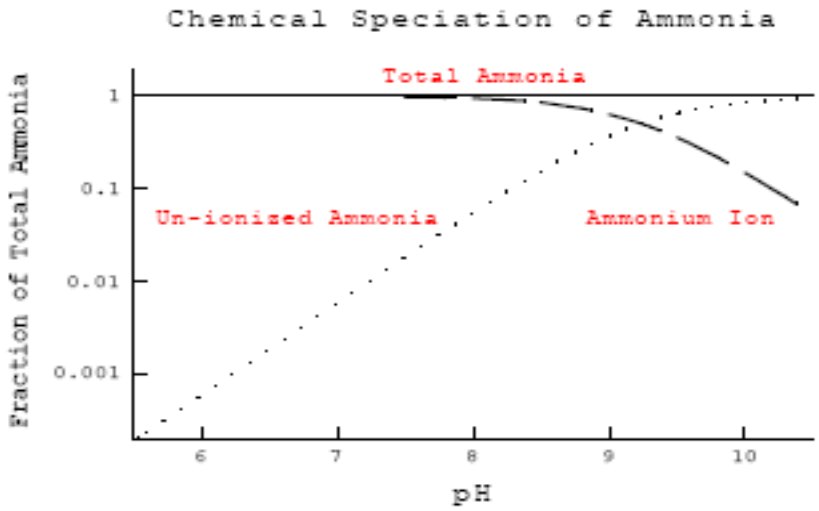


Figure 1. Fraction of Chemical Species of Ammonia Present with Change in pH (at 25°C).

Each separate fraction of total ammonia can be calculated in freshwater from the Henderson-Hasselbach equation if the pH and p*Ka* are known:

NH_4^+ = Total ammonia/(1+ antilog (pH-p*Ka*)) = Total ammonia – NH_3 (Wood 1993)

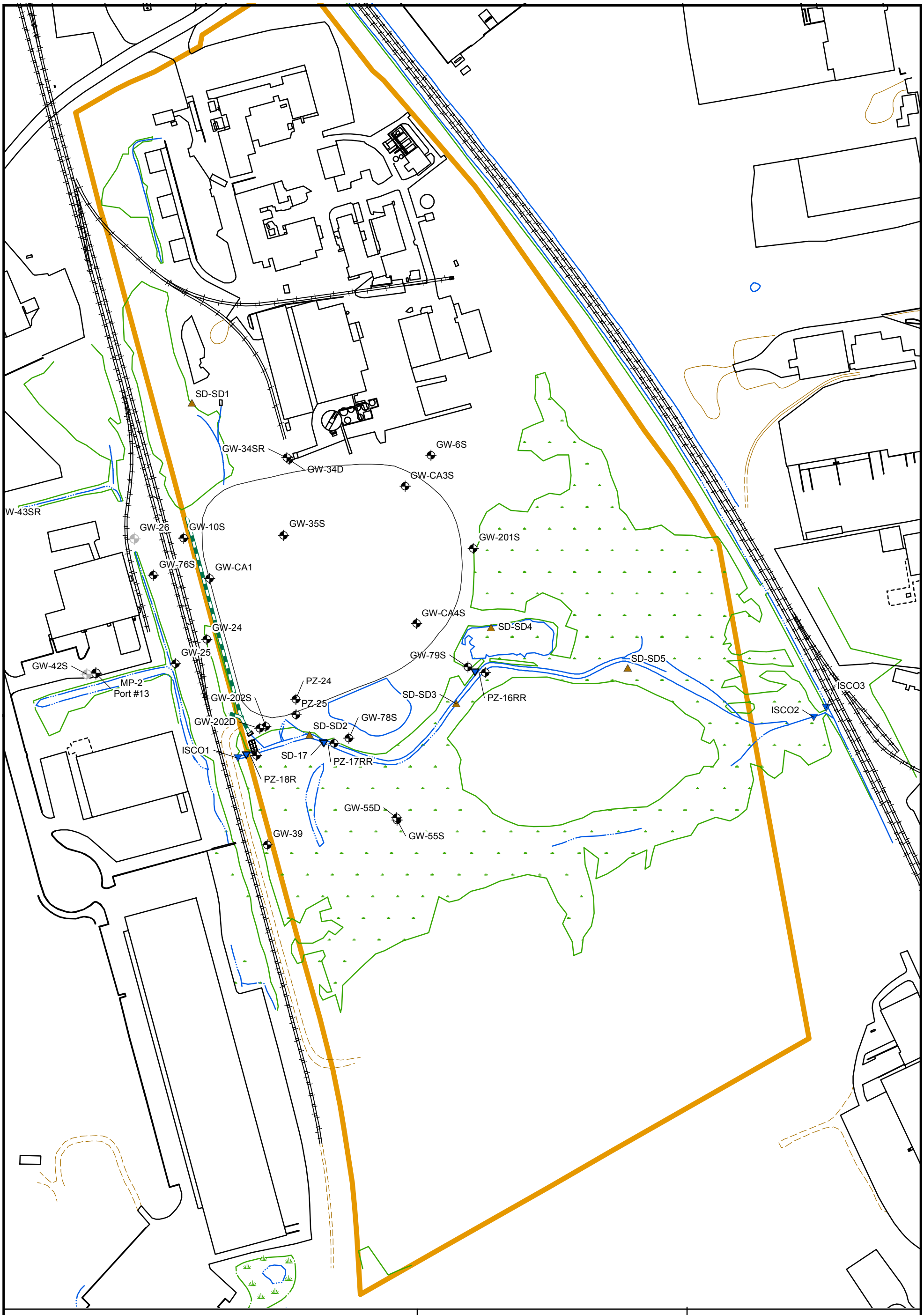
and,

p*Ka* = 0.09018 + (2729.92/(273.2 + T)) (Emerson et al. 1975)

where T is temperature in °C.

ATTACHMENT C

INTERIM RESPONSE STEPS WORK PLAN SURFACE WATER SAMPLE LOCATIONS FIGURE EXTRACTED FROM JULY 2019 SEMI-ANNUAL REPORT FOR OLIN CHEMICAL SUPERFUND SITE



\\WFD-FS1\projectf$\Projects\old_Wakefield_Data\projects\OLIN\Wilmington\GIS\MapDocuments\Interim Response Work Plan\Olin_IRWP2.mxd June 07, 2018 DWN: emily.gardiner CHKD: AKN